

# Surface nanopatterning of metal thin films by physical vapour deposition onto surface-modified silicon nanodots

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## Abstract

Nanostructuring of metallic and semiconductor surfaces in the sub-100 nm range is a key point in the development of future technologies. In this work we describe a simple and low-cost method for metal nanostructuring with 50 nm lateral and 6 nm vertical resolutions based on metal film deposition on a silane-derivatized nanostructured silicon master. The silane monolayer anti-sticking properties allow nanopattern transfer from the master to the deposited metal films as well as easy film detachment. The method is non-destructive, allowing the use of the derivatized master several times without damaging. Potential applications of the method are in the field of high-density data storage, heterogeneous catalysis and electrocatalysis, microanalysis (sensors and biosensors) and new optical devices.

## 1. Introduction

The development of large-scale fabrication methods of structured surfaces with feature sizes in the nanometre range is still a constant challenge in the nanotechnology community. An accurate control of the surface topography would promote a great impact on the materials science field. For example, it is well known in the biomedical materials research area that the shape of a surface controls its interaction with biological components, as has been recently noted [1]. In order to bring new alternatives to this key issue, numerous strategies, such as electron-beam lithography, self-assembling methods, soft lithography and others, have been designed. But each of those methods has advantages and disadvantages depending on the minimum feature size, the degree of ordering or the material to be used.

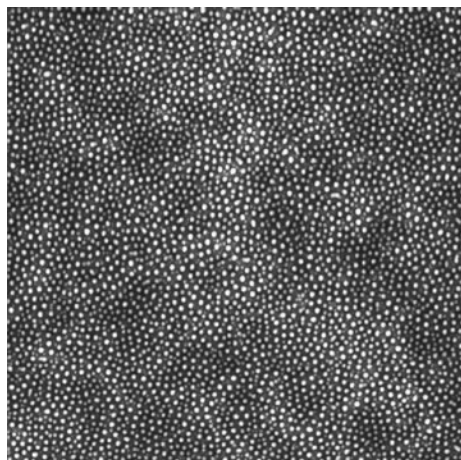
In particular, for the case of nanostructured metal surfaces, novel and interesting routes have been developed in recent

years, such as imprinting with a nanoporous alumina [2], two-step replication, colloidal templating techniques or ion sputtering. This interest arises from the particular properties developed by the nanostructured metal surfaces, such as tribological properties (wear) or their interaction with electromagnetic radiation, which could be used for developing diverse technologies [3, 4].

Large-scale fabrication of nanostructured metal surfaces by ion sputtering surface erosion has proved to be a very valuable and useful technique [5]. By this procedure nanodotted patterns and ripple structures along any desired direction can be achieved both on metals [6] and semiconductor surfaces [7, 8]. Although the method has demonstrated itself to be a powerful alternative for producing accurate nanopatterns, it has the disadvantage of being aggressive (i.e. a single crystal must be eroded for preparing each nanopatterned surface), making the method unsuitable for serial fabrication.

In this work we present a novel approach, that merges the strategy of using irradiation techniques for producing large-scale nanopatterned surfaces in an accurate manner with

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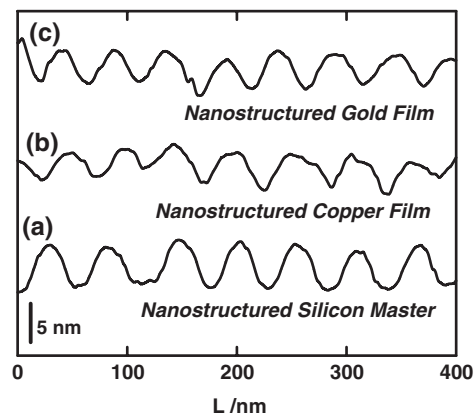
**Figure 1.** A  $3 \times 3 \mu\text{m}^2$  top view AFM image of the nanostructured silicon master surface.

moulding procedures, commonly used in serial fabrication, in order to design a route for large-scale serial fabrication of nanostructured metal surfaces. This method allows the fabrication of nanostructured surfaces consisting of high-density arrays of nanoholes on copper and gold films.

## 2. Experimental procedure

Nanostructured silicon samples were used as masters for the patterning of different metallic films since silicon is an extremely stable material that resists different chemical environments and thermal conditions. The nanostructured silicon masters were prepared by ion sputtering of single-crystal n-type Si(100) wafers [8]. The substrates were cleaned sequentially in ultrasonic baths with trichloroethylene, acetone and methanol before the nanostructuring procedure. The ion sputtering was done in a high-vacuum chamber with a base pressure of  $2 \times 10^{-7}$  mbar by irradiation with 1.2 keV  $\text{Ar}^+$  ions impinging normally on the silicon surface for 10 min. As already reported, this procedure results in the formation of short-range hexagonal ordered arrays of silicon nanodots (figure 1). The nanostructured silicon samples were treated for 20 min with Piranha solution ( $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ ) to build up an ultra-thin and homogeneous  $\text{SiO}_2$  layer on the Si. This procedure does not promote severe changes on the nanodot morphology. Afterwards, the samples were rinsed copiously with Milli-Q<sup>TM</sup> water, dried with  $\text{N}_2$  and immediately derivatized by immersion in a solution  $4 \times 10^{-3}$  M in octadecyltrichlorosilane (OTS) for one hour. This procedure results in the formation of an OTS self-assembled monolayer on the master surface. The surface-modified silicon master was sonicated on pure hexane during 10 min to remove the physisorbed OTS molecules remaining on the template surface. It should be noted that the presence of physisorbed OTS molecules could be transferred to the further deposited metallic films introducing severe distortions in the nanopattern.

Metallic films (copper, gold) were deposited on the OTS-covered silicon in a vacuum evaporator at a pressure of  $\sim 10^{-7}$  mbar with the substrate kept at room temperature; that is, with no intentional sample heating. Electrochemical deposition was made in a conventional three-electrode glass-cell using the deposited metallic films on the silicon



**Figure 2.** Cross-section analysis showing the dimensions of the features transferred from the nanostructured silicon master (a) to a copper (b) and gold (c) films.

master as the working electrode, a large copper plate as counter-electrode and a saturated calomel electrode as reference electrode. The plating bath consists of 0.6 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5 \text{ M H}_2\text{SO}_4 + 2.5 \times 10^{-5}$  M thiourea. The copper electrodeposition process was carried out under galvanostatic conditions at  $20 \text{ mA cm}^{-2}$  and  $25^\circ\text{C}$ .

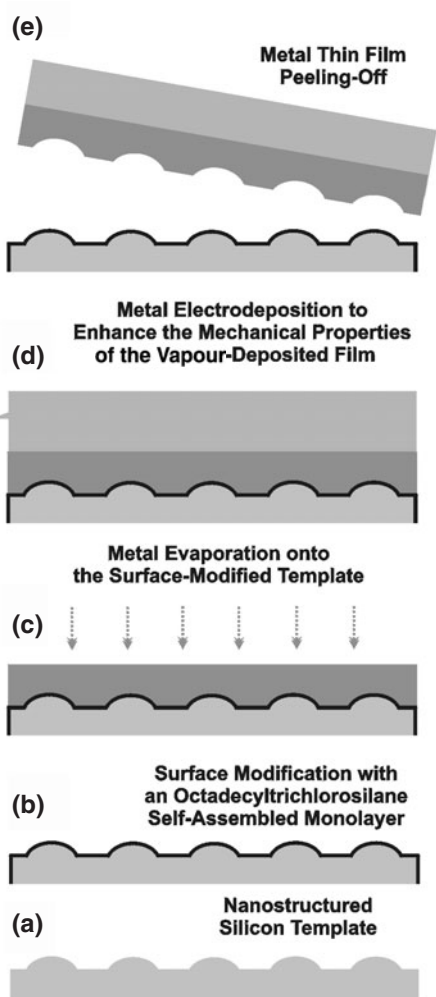
The silicon master and the nanostructured metals surfaces were imaged by atomic force microscopy (AFM) operating in tapping mode.

## 3. Results

A typical AFM image of the silicon master is shown in figure 1. The surface exhibits a short-range hexagonal ordered array of *nanodots* with a density of dots close to  $10^{11}$  dot  $\text{cm}^{-2}$ . A cross-section analysis of the AFM images reveals dots of 40 nm in average size and 6 nm in average height (figure 2(a)).

A scheme of the complete procedure involved in nanopattern transfer by using our method is shown in figure 3. The  $\text{SiO}_2$  surface of the master (figure 3(a)) was chemically modified by immersion in the OTS-containing hexane solution for 1 h (figure 3(b)). Then, a 200 nm thick metallic film was deposited by physical vapour deposition (PVD) on the OTS-covered silicon master (figure 3(c)). After depositing this metal film, a thicker copper film (5–10  $\mu\text{m}$  thick) was electrodeposited onto it (figure 3(d)) in order to enhance the metal film mechanical stability before detachment. Finally, the entire film was easily removed from the template by using tweezers without damaging the nanopatterned sample or the template surface (figure 3(e)).

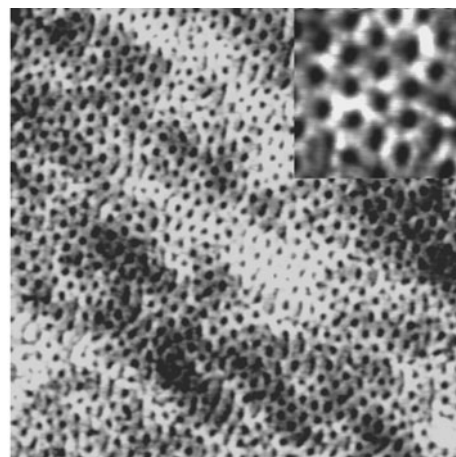
Typical examples of the inner interfaces of the metallic films (those in contact with the OTS-covered silicon master) after detachment are shown in figures 4 and 5. The AFM images show a large-scale patterning of copper (figure 4) and gold (figure 5) surfaces consisting of short-range hexagonal ordered arrays of *antidots*. The corresponding cross-sections (figures 2(b), (c)) show the accurate way in which the master features are transferred to the metallic surfaces. From an analysis of these images it can be concluded that the lateral and vertical resolutions of this method are at least 50 and 6 nm, respectively. The inset in figure 4 reveals in more detail the hexagonal symmetry of the *antidot* array, and the



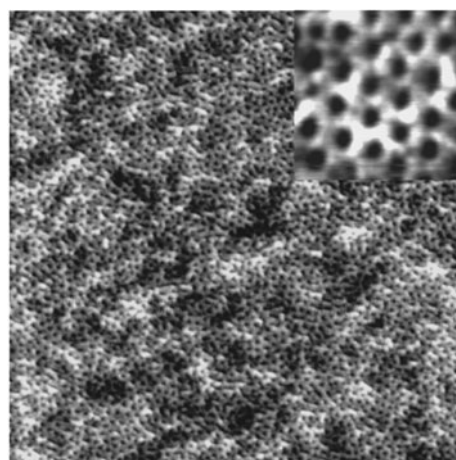
**Figure 3.** Scheme showing the different steps involved in the nanostructuring method. (a) Silicon template, (b) surface master derivatization with the OTS-monolayer, (c) metal PVD on the OTS-derivatized silicon master, (d) copper electrodeposition onto the PVD metal film/OTS-silicon, (e) detachment of the patterned metallic film.

small metallic grains that constitute the building blocks of these films. It should be stressed that the small grain size ( $\approx 15$  nm) and low surface roughness ( $< 2$  nm) of the metallic deposit are extremely important to achieve the 50 nm lateral and 6 nm vertical resolution limits.

The images displayed in the figures are representative of the nanopatterning process at the submicrometre and nanometre ranges. Similar images were obtained at different spots of the moulded sample within the geometrical range, 3–6 mm, in which the original silicon template was nanostructured [8]. For larger image sizes, 10–30  $\mu\text{m}$  wide, the overall surface was still quite smooth although some imperfections, such as protrusions or holes, can be found. These imperfections could arise from imperfections of the OTS monolayer that were not totally removed by the sonication process. It should be noted that, for instance, the moulded gold films have been successfully used as templates to obtain from them, following a similar nanopatterning process, nanodotted patterns on metallic surfaces [9]. Finally, it should be stressed that this method by itself does not induce any special order in



**Figure 4.** A  $2.2 \times 2.2 \mu\text{m}^2$  top view AFM image of a nanopatterned copper film. The inset shows a zoomed region where hexagonal arrays of nanoholes and the small copper grains that form the building blocks of the patterned surface are evident.



**Figure 5.** A  $3.7 \times 3.7 \mu\text{m}^2$  top view AFM image of a nanopatterned gold film. The inset shows a zoomed region where hexagonal arrays of nanoholes and the small gold grains that form the building blocks of the patterned surface are evident.

the metallic nanopattern. In fact, it does preserve or transfer the original ordering of the silicon template on the final metal film nanopattern. In this case, since the original template displays short-range hexagonal order [8], the same ordering is observed in the moulded surfaces. Were the original template to have a high degree of order, our results suggest that a similar ordering would be preserved on the nanopatterned metallic film.

The OTS layer plays a crucial role in this method because it allows:

- (i) conformal growth of the depositing layer that enables the nanopattern transfer with high resolution;
- (ii) easy detachment of the nanopatterned film.

In fact, when this procedure (i.e. the derivatizing step in figure 3(b)) is skipped the patterned sample is heavily damaged during the detachment process.

Among the advantages of this method we can mention its simplicity and low-cost and non-destructive character. Thus, the same original master can be repetitively used at

least 15–20 times. Moreover, it allows large-scale patterning with high lateral and vertical resolution using the master several times. Finally, another important advantage of the method is its high versatility, since it is compatible with different deposition methods (PVD, chemical vapour deposition, electroless, electrodeposition) currently used for material patterning.

However, it is important to bring attention to some issues related to this method. First, OTS molecules physisorbed on the master surface could be transferred to the nanopatterned metallic film. Under these conditions the quality of the transfer process becomes degraded. However, this problem can be minimized by simple sonication of the master in hexane. The main limitation of this method is related to the thermal stability of the OTS layer. Since it is stable only up to 400 °C, those film deposition processes involving elevated working temperatures are not suitable for this nanopatterning strategy.

Direct application of metal nanopatterning by this method could be related to future information storage technologies since these metallic nanostructures are stable under the repetitive reading with AFM tips [10]. Other possible applications of this method are in the area of heterogeneous catalysis and the development of smaller and more efficient sensors and biosensors.

#### 4. Conclusions

Chemical modification of nanostructured silicon surfaces by silane monolayers can be used as a simple and low-cost strategy for large-scale metal nanopatterning. We have demonstrated that a high density of ordered sub-50 nm silicon structures can be accurately and easily transferred to a variety of metals by previously depositing an OTS layer on the nanostructured

silicon surface. This layer plays a key role since it enables the conformal growth of the depositing film and its further detachment, and allows nanopattern transfer with both high vertical and lateral resolutions. The non-destructive character and versatility of this method make it a promising route for surface nanopatterning with technological applications.

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